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(54) Title: A METHOD FOR THE PRODUCTION OF ESSENTIALLY UNBRANCHED OCTENES AND DODECENES BY OLIGOMERIZING UNBRANCHED BUTENES.		
<p>(57) Abstract:</p> <p>A method for the production of essentially unbranched octenes and dodecenes by oligomerizing hydrocarbon flows that contain butene-1 and/or butene-2 and butane and that basically contain no iso-butene at temperatures of between 30 and 280 °C and at a pressure of between 10 and 300 bar on a catalyst that contains nickel, in which case one returns such quantities of the butane separated from the reaction mixture and of the unreacted butene to the oligomerization reaction that the maximum oligomer content in the reacted reaction mixture does not exceed 25% by weight at any point in the reactor or - in the case one uses a reactor cascade - at any point in the reactor cascade.</p>		

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A method for the production of essentially unbranched octenes and dodecenes by oligomerizing unbranched butenes.

Description

The invention concerns the oligomerization of butene-1 and/or butene-2 to form essentially linear octenes and dodecenes in the presence of a heterogeneous catalyst that contains nickel, in which case a concentration of not more than 25% by weight for the formed oligomers is maintained in the reaction mixture.

Olefins with between 2 and 6 carbon atoms and their mixtures, particularly olefins with 4 carbon atoms, are available in large quantities from FCC-units as well as from steam crackers. After separating the iso-butene, the respective C₄-section, i.e., the mixture of butenes and butanes, is very well suited for the preparation of oligomers and particularly of octenes and dodecenes. The octenes as well as the dodecenes can be used for the production of softening agents after the hydroformylation and subsequent hydration to form the respective alcohols.

Regarding their use as softener alcohol, the degree of branching plays a major role for the softener properties. The degree of branching is described with the ISO-index that indicates the average number of methyl branchings in the respective fraction. For example, n-octene adds 0, methyl heptene adds 1 and dimethyl hexene adds 2 to the ISO-index. A lower ISO-index indicates that the molecules in the respective fraction are more linear. The ISO-index gets lower with an increasing linearity and this results in higher yields in the oxation and better properties for the thus produced softening agents.

The large-scale oligomerization is carried-out in a homogeneously or heterogeneously catalytic manner.

The homogeneously catalytic working method has been thoroughly described by A. Chauvel and G.Lefebvre in *Petrochemical Processes*, Vol. 1, Editions Technip (1989), page 183 through 187.

The homogeneously catalytic process has the disadvantage that the catalyst must be separated from the reaction mixture. This separation phase creates waste flows that must be processed again according to environmental regulations. Finally, the homogeneous catalyst cannot be regenerated.

However, such disadvantages do not exist for the heterogeneously catalytic olefin oligomerization. The Octol process developed by the companies UOP and Hüls AG represents a method that is used for large-scale applications; in this process, C₃- and C₄-olefins are reacted to form higher olefins at temperatures of between 30 and 250 °C and at pressures of between 20 and 80 bar on a catalyst consisting, for example, of phosphoric acid applied to SiO₂ as the carrier material. This process was described, for example, in *Petrochemical Processes loc.cit.* and in *Hydrocarbon Processing*, February 1992, pages 45/46.

Furthermore, it is known from DE-A 43 39 713 that the butene oligomerization can be performed in a preferred manner and with a very good selectivity in relation to linear products with the use of catalysts that contain specific nickel types.

While the homogeneously catalytic process exhibited the above-mentioned disadvantages regarding catalyst use and the heterogeneously catalytic Octol process produced few linear products when using acid catalysts, the method in accordance with DE-A 43 39 713 was worthy of an improvement with respect to catalyst service life and selectivity for the octene formation.

Accordingly, the task of the invention consisted in finding a heterogeneously catalytic method that results in a long catalyst service life at a very good yield and high selectivity for the formation of oligomers with little branching.

In accordance with the invention, this task was solved with a method for the production of essentially unbranched octenes and dodecenes by oligomerizing hydrocarbon flows that contain butene-1 and/or butene-2 and butane and are essentially free from iso-butene at temperatures of between 30 and 280 °C and at a pressure of between 10 and 300 bar on a heterogeneous catalyst that contains nickel, in which case one returns such a quantity of the butane separated from the reaction mixture and of unreacted butene to the oligomerization reaction that the maximum oligomer content in the unreacted reaction mixture never exceeds 25% by weight and preferably 20% by weight at any point of the reactor or - when using a reactor cascade - at any point of the reactor cascade.

In this application, "oligomers" stands for dimers, trimers and higher oligomers of butene-1 and/or butene-2.

It has been shown that this method permits an execution of the butene oligomerization with a reaction yield of more than 70% with a simultaneous C₈-selectivity of more than 80%. In addition to the good reaction yield and selectivity values, maintaining the concentration limits also results in a longer catalyst service life, since the formation of high-boiling compounds that are deposited on the catalyst surfaces and thus cause a decrease in the catalyst activity level is suppressed.

Although a return ("C₄-recycle") is indicated in a general form already for the homogeneously catalytic method and for the Octol process, this obviously occurs to a lesser degree than in the presented method and without achieving the advantageous results in accordance with the invention.

Accordingly and in accordance with the reference Petrochemical Processes, page 185, the unreacted C₃-C₄-hydrocarbons (together with the undesirable high-boiling substances) are returned "to serve as diluents and to avoid excess conversions that would cause a drop in selectivity". In contrast to the above, the method in accordance with the invention produces high yields and a high selectivity.

Figure 1 on page 45 in Hydrocarbon Processing, February 1992, indicates that a C₄-recycling occurs. It is obvious, however, that the return occurs to a lesser degree, i.e., in quantities that must result in concentrations of more than 25% by weight of oligomers in the reaction mixture, since the

reaction is performed in a quasi-isothermal manner, while the relatively large liquid gas quantity to be returned in accordance with the invention permits a technically simpler quasi-adiabatic working method.

Suitable catalysts consist of catalysts that generally contain Nickel and are known to produce only a minor branching like those described by O'Connor et al. in *Catalysis Today*, 6, 329 (1990), particularly on pages 336-338 and also in the references listed in the DE-A 4 339 713 regarding prior art, in which case reference is made here explicitly regarding the literature indicated there.

As catalyst examples shall be mentioned in this connection nickel on silicon dioxide, nickel on silicon dioxide-aluminum oxide, nickel on silicon dioxide-aluminum oxide-layer silicates such as mica and oxides of aluminum, particularly montmorillonite, nickel on zeolite carriers such as mordenite, faujasite, zeolite X, zeolite Y, zeolite ZSM-5 or other zeolites of the ZSM-type, zeolites with a MCM-41 structure or with a CZS-1 structure and also nickel on aluminum oxide, nickel on zirconium oxide that has been treated with acids such as sulfuric acid, phosphoric acid or boric acid, $\text{NiO}_2/\text{ZrO}_2/\text{SO}_4/\text{SiO}_2$, as well as nickel on sulfated titanium oxide, in which case the nickel material of these catalysts is generally present in the form of NiO .

According to a preferred example of the method in accordance with the invention, the oligomerization is performed in the liquid phase and with the use of the catalysts described and claimed in DE-A 43 39 713. Reference is made here explicitly to this patent document and its information is considered incorporated here.

The catalytically active mass of the catalysts described there basically consists of nickel oxide, silicon dioxide, titanium dioxide and/or zircon dioxide and possibly of aluminum oxide, i.e., without considering the contaminants that were introduced through initial or process chemicals during the production of the catalysts. These catalysts contain between 10 and 70% by weight nickel oxide, between 5 and 30% by weight titanium dioxide and/or zircon dioxide, between 0 and 20% by weight aluminum oxide and the rest to reach 100% by weight consists of silicon dioxide and they are obtained by precipitating the catalyst mass at a pH-value of 5-9 by adding an aqueous solution that contains nickel nitrate to an alkali water glass solution that contains titanium and/or zircon dioxide and by a filtering, drying and tempering at between 350 and 650 °C.

The catalysts are preferably arranged on a solid bed and thus preferably consist of solid pieces such as pellets (5 mm x 5 mm, 5 mm x 3 mm, 3 mm x 3 mm), rings (7 mm x 7 mm x 3 mm, 5 mm x 5 mm x 2 mm, 5 mm x 2 mm x 2 mm) or strands (1.5 mm diameter, 3 mm diameter, 5 mm diameter). The above sizes represent just examples and do in no way restrict the object of this invention.

The method in accordance with the invention is individually performed by reacting a hydrocarbon flow that contains butene-1, butene-2, butane and not more than small quantities of iso-butene, preferably in the liquid phase, on the above-mentioned catalysts that contain NiO .

Suitable C₄-hydrocarbon flows may consist of mixtures with the following composition:

Butane	10 to 90% by weight
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Butene	10 to 90% by weight
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in which case the butene fraction may have the following composition:

butene-1	1 to 50% by weight
butene-2-cis	1 to 50% by weight
butene-2-trans	1 to 99% by weight
iso-butene	1 to 5% by weight

The so-called Raffinate II is considered a particularly preferred material to be used, i.e., a C₄-hydrocarbon mixture that contains butene and is obtained from the C₄-section from crackers after the separation of higher unsaturated hydrocarbons such as diolefins, particularly 1,3-butadiene, or of acetylene and subsequently of the iso-butene contained in it. The following shows a typical composition of Raffinate II:

iso- and n-butane	26% by weight
iso-butene	1% by weight
butene-1	26% by weight
butene-2-trans	31% by weight
butene-2-cis	16% by weight

Butadienes and compounds that contain sulfur and oxygen such as alcohols, aldehydes, ketones or ethers can be removed from the C₄-hydrocarbon flows through a selective hydration or absorption on molecular sieves as indicated in DE-A 39 14 817.

The oligomerization reaction is generally run at temperatures of between 30 and 280 °C, preferably of between 30 and 140 °C and particularly preferred of between 40 and 130 °C, and at a pressure of generally between 10 and 300 bar, preferably of between 15 and 100 bar and particularly preferred of between 20 and 70 bar. In that regard, the pressure is selected appropriately in such a manner that the utilized hydrocarbon mixture is present in the liquid phase or in an above-critical state at the adjusted temperature. The reactor generally consists of a cylindrical reactor in which the catalyst is placed and through which the liquid reaction mixture flows from the top to the bottom, for example. The oligomerization method in accordance with the invention can be run in an individual reactor until the final butene yield has been reached, in which case the oligomerization catalyst can be arranged in a single or in several solid beds in the reactor. As an alternative, the method in accordance with the invention can also be performed in a reactor cascade consisting of several and preferably of two reactors arranged in series, in which case the butene oligomerization in the reaction mixture is run only to a partial yield when passing through a reactor or through cascade reactors located upstream of the last reactor or reactors and the end yield is achieved only when the reaction mixture passes through the last cascade reactor. The oligomerization catalyst can be arranged in a single or in several solid catalyst beds in the individual reactors of the reactor cascade.

Furthermore, different reaction conditions for pressure and/or temperature can be set in the individual reactors of the reactor cascade within the scope of the above-mentioned pressure and temperature ranges. Although it is preferred to use the same catalyst in all reactors of the cascade, it is also possible to use different oligomerization catalysts in the individual reactors of the cascade. The term "single-stage reaction zone" will be used in the following when using a single oligomerization reactor and also when using a reactor cascade, in whose reactors the same

oligomerization catalyst is used, and the term "multi-stage reaction zone" will be used in the following when different oligomerization catalysts are used in the individual cascade reactors.

When a single oligomerization reactor is used, the returned C₄-hydrocarbon mixture that contains little butene and mainly butane is preferably mixed with the hydrocarbon mixture prior to its entering the reactor; however, it is also possible to feed the hydrocarbon mixture and the recycled C₄-hydrocarbon mixture to the oligomerization reactor through separate pipes. When the catalyst is arranged in several solid beds in the oligomerization reactor, the recycled hydrocarbon flow can be divided and supplied to the reactor at several points, e.g., upstream of the first solid bed in the flow direction of the reaction mixture and/or between the individual catalyst beds. The same applies to the use of a reactor cascade, in which case the returned hydrocarbon flow can be fully supplied to the first cascade reactor or can be supplied through several feed pipes to the individual cascade reactors as was described for the single reactor. After leaving the single- or multi-stage reaction zones, the formed oligomers are in a generally known manner separated from the unreacted C₄-hydrocarbons and these C₄-hydrocarbons are completely or almost completely returned, i.e., in any case with such a quantity that the oligomer content in the reacted reaction mixture does not exceed 25% by weight and preferably 20% by weight at any reactor point or - when using a reactor cascade - at any cascade reactor point. In other words: The recycling of the C₄-hydrocarbon mixture shall be controlled such that the oligomer content in the reacted reaction mixture does not exceed 25% by weight or preferably 20% by weight at any reactor point or - when using a reactor cascade - at any cascade reactor point and the oligomer content in the reacted reaction mixture preferably never falls below 10% by weight at the reactor outlet or - when using a reactor cascade - at the cascade reactor outlet. To achieve such an oligomer content in the reacted reaction mixture, one generally sets a weight ratio between return flow and freshly supplied hydrocarbon flow of between 0.5 and 10, preferably of between 1 and 7 and particularly preferred of between 1 and 4, in which case this information relates to the stationary state of the reaction system.

There basically exists no lower limit for the oligomer content in the reaction mixture; however and when selecting a very low oligomer content, the method becomes uneconomical due to the fact that the required return flow becomes excessively large. For that reason, one does generally not go below a lower limit of 10% by weight oligomers in the reacted reaction mixture and prior to its processing.

In contrast to the isothermal reaction, in which the heat created in an isothermal reaction is removed by a cooling with cooling or temperature control devices such as temperature control baths, cooling jackets or heat exchangers and the reactor temperature is thus maintained at a constant level, i.e., isothermal, the adiabatic reaction refers to an operation, in which the heat released in an exothermal reaction is absorbed by the reaction mixture in the reactor and there occurs no cooling with cooling devices. It is only natural that a purely adiabatic reaction within a theoretical / academic interpretation of the term "adiabatic" can be achieved technically only with an uneconomical effort, since a -negligibly small - part of the heat released during the exothermal reaction is in an unavoidable manner also absorbed by the reactor body and is transferred to the environment through heat conduction and heat dissipation. Accordingly and from a technical point of view, an adiabatic reaction or operation refers to a reaction or operation, in which the whole reaction heat is absorbed by the reaction mixture and is discharged with it from the reactor, i.e.,

with the exception of the part of the reaction heat that is transferred to the outside through a natural heat conduction and heat dissipation process. The term "quasi-adiabatic" reaction is thus and from a technical point of view used synonymously with the term "adiabatic reaction". Accordingly, the measure of an adiabatic reaction like the one used in this invention corresponds to an adiabatic reaction within the technical explanation given earlier. In contrast to this adiabatic reaction, an isothermal reaction or operation forces the removal of the reaction heat from the reactor with cooling and temperature control devices in a targeted manner and in addition to the natural heat conduction and dissipation process, in which case the reaction heat is initially and generally absorbed by a heat carrier medium, the cooling agent, prior to releasing it into the environment or - when using heat exchangers - prior to using this heat to heat substances or to produce energy. It is only natural that one must distinguish between an isothermal reaction within the technical scope and an isothermal reaction within a theoretical / academic scope, since a - negligibly small - part of the reaction heat will be removed in a practically unavoidable manner with the heated reaction mixture, thus making it possible to synonymously speak of a "quasi-isothermal" reaction within a technical interpretation.

Since the exothermal reaction created in the case of this oligomerization method is based solely on the contact between the butene and the oligomerization catalyst and heat is thus released only in the area of the catalyst fill, the reaction temperature in the catalyst fill and thus also the reactor temperature can basically be regulated with the reactant feed. The catalyst fill temperature increases with an increasing butene reaction on the catalyst, i.e., the reaction temperature increases. Since no heat is removed through cooling devices in such an adiabatic operation, practically all of the reaction heat created during the oligomerization is removed by the reaction mixture that flows through the catalyst fill. Such an operation without additional measures and with the hydrocarbon mixture to be utilized in accordance with the invention would severely limit the throughput and thus the yield per time unit in relation to the volume unit of the oligomerization catalyst used, since the reaction temperature would increase substantially when increasing the yield, thus causing a higher formation of secondary products and - in a worst-case scenario - an uncontrolled reactor runaway with a subsequent butene polymerization, an overheating and an irreversible catalyst damage.

It was found that the above-described measure to return the unreacted C₄-hydrocarbons that have been separated from the oligomer product to the oligomerization reactor or possibly to the reactor cascade used for the oligomerization makes it possible to maintain the reaction temperature in the catalyst fill within the desired temperature range even at a high butene yield and to achieve a high selectivity for the desired oligomerization products. Since the C₄-hydrocarbon that was returned to the oligomerization reaction and was not reacted exhibits a lower content of reactive butene and a higher content of butanes that are inert under the reaction conditions than the hydrocarbon flow that was freshly supplied to the oligomerization reactor, the return flow mixed with this flow actually dilutes it with inert butanes that also contribute to the reaction heat removal from the catalyst fill. Accordingly, the oligomerization can be run in the oligomerization reactor under adiabatic conditions, i.e., without requiring cooling devices in the reactor as is the case for an isothermal operation, by removing the reaction heat with the reaction mixture.

The reaction in accordance with the invention also exhibits the peculiar property that the process can be executed in a quasi-adiabatic manner, since the heat density in the reactor can be controlled at will by diluting the returned hydrocarbon flow and by selecting the quantity and temperature of this flow. Prior to its mixing with the freshly supplied hydrocarbon flow or - in the case of a direct feed to the oligomerization reactor - prior to its metering, the returned hydrocarbon flow can be cooled to a lower temperature, thus resulting in an additional improvement of the reaction heat removal. The quasi-adiabatic operation also includes a method configuration, in which the butene reaction to form oligomers is divided in a reactor cascade consisting of two or several and preferably of two oligomerization reactors and the partially reacted reaction mixture is cooled after leaving one reactor and prior to entering the next reactor with conventional cooling devices such as cooling jackets or heat exchangers. The adiabatic method substantially reduces equipment cost in comparison with the isothermal process.

Through the return of unreacted butene with the return flow to the oligomerization reactor, one achieves a high utilization rate for the butene that is supplied with the hydrocarbon to the oligomerization reactor for the oligomerization. Furthermore, the quasi-adiabatic operation permits a high butene yield with a simultaneously high selectivity.

The oligomer separation is achieved in a generally known manner through a fractionated distillation, particularly in the desired octene and dodecene fractions that serve as initial materials for the hydroformylation performed to produce the softening agent alcohols nonanol and tridecanol. Based on the reduced branching of the initial oligomers, the alcohols prepared from it exhibit excellent properties for the production of softening agents.

The method in accordance with the invention will be explained in more detail with the following examples.

Examples

Examples 1 through 4

The tests were run continuously in an isothermal reactor (length of approx. 1.5 m, 30 mm diameter) at 20 bar and at 80 °C. A Raffinate II of the following composition was used:

iso-butane	3% by weight
n-butane	15% by weight
iso-butene	2% by weight
butene-1	30% by weight
butene-2-trans	32% by weight
butene-2-cis	18% by weight

The catalyst material was prepared in accordance with DE-A 43 39 713 and was processed to form 5 mm x 5 mm pellets. Composition in % by weight of the active components: 50% by weight NiO, 12.5% by weight TiO₂, 33.5% by weight SiO₂, 4% by weight Al₂O₃.

One obtained the following results (after reaching the stationary state of the reaction):

Example	1 (reference)	2	3	4
Throughput (kg _{RaffII} /(l _{cat} ·h))	0.75	0.75	0.5	0.375
C ₄ -return/Raff. II (weight/weight)	0	1	1.5	2
[C ₈ ⁺] reactor discharge (% by weight)	42.6	24.3	22.3	20.0
C ₄ -yield in relation to the butenes contained in the Raffinate II (% by weight)	52.0	59.2	67.9	73.1
Selectivity (% by weight)				
C ₈	76.9	81.7	81.5	81.4
C ₁₂	18.4	14.8	14.9	15.1
C ₁₆₊	4.7	3.5	3.6	3.5
C ₈ -Iso-Index	0.97	0.95	0.94	0.93

Example 5

The tests were performed continuously at 30 bar in a reactor cascade consisting of two adiabatically operated reactors with an intermediate cooling (length of 2 x approx. 4 m, diameter of 80 cm). A Raffinate II of the following composition was used:

iso-butane	2% by weight
n-butane	10% by weight
iso-butene	2% by weight
butene-1	32% by weight
butene-2-trans	37% by weight
butene-2-cis	17% by weight

The catalyst material was prepared in accordance with DE-A 43 39 713 and was processed to form 5 mm x 5 mm pellets. Composition in % by weight of the active components: 50% by weight NiO, 12.5% by weight TiO₂, 33.5% by weight SiO₂, 4% by weight Al₂O₃.

One obtained the following results (after reaching the stationary state of the reaction):

Throughput (kg _{RaffII} /(l _{cat} ·h))	0.375
C ₄ -return/Raffinate II (weight/weight)	3
Inlet temperature at first reactor (°C)	38
Outlet temperature at first reactor (°C)	67
Inlet temperature at second reactor (°C)	60
Outlet temperature at second reactor (°C)	75
[C ₈ ⁺] reactor discharge (% by weight)	18.3
C ₄ -yield in relation to the butenes contained in the Raffinate II (% by weight)	83.1
C ₈ -Selectivity (% by weight)	83.3
C ₈ -Iso-Index	1.00

Patent claims

1. A method for the production of essentially unbranched octenes and dodecenes by oligomerizing hydrocarbon flows that contain butene-1 and/or butene-2 and butane and contain basically no iso-butene at temperatures of between 30 and 280 °C and at a pressure of between 10 and 300 bar on a catalyst that contains nickel, characterized by the fact that one returns such quantities of the butane separated from the reaction mixture and of the unreacted butene to the oligomerization reaction that the maximum oligomer content in the reacted reaction mixture does not exceed 25% by weight at any point in the reactor or - in the case of a reactor cascade - at any point in the reactor cascade.
2. A method in accordance with claim 1, characterized by the fact that the oligomerization is performed in the liquid phase.
3. A method in accordance with claim 1, characterized by the fact that the oligomer content in the reacted reaction mixture does not exceed 25% by weight at any reactor point or - when using a reactor cascade - at any cascade reactor point and that the oligomer content in the reacted reaction mixture preferably never falls below 10% by weight at the reactor outlet or - when using a reactor cascade - at the cascade reactor outlet.
4. A method in accordance with claim 1, characterized by the fact that the reaction heat is absorbed by selecting the quantity and temperature of the return flow and the oligomerization is run in an adiabatic or in an essentially adiabatic manner.
5. A method in accordance with claim 1, characterized by the fact that the oligomerization is performed above a solid bed catalyst that essentially consists of NiO, SiO₂, TiO₂ and/or ZrO₂ and possibly of Al₂O₃.
6. A method in accordance with claim 1, characterized by the fact that one performs the oligomerization above a solid bed catalyst that essentially contains between 10 and 70% by weight NiO, between 5 and 30% by weight TiO₂ and/or ZrO₂, between 0 and 20% by weight Al₂O₃ and SiO₂ as the rest to reach a total of 100%.
7. A method in accordance with claim 1, characterized by the fact that the oligomerization is run in a reactor cascade.

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